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ELECTROLYTIC PREPARATION OF HIGH DIELECTRIC FILMS

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FOREWARD

The work described in this report was carried out under contract NASw-969 for the NASA Headquarters, Washington 25, D.C. The program is directed toward the development of high dielectric thin films by electrolytic techniques.

The authors would like to acknowledge the contribution of R. D. Wales for the development of the isopropyl alcohol bath.

ABSTRACT

12838

The first quarterly report on the preparation of high dielectric films is primarily concerned with procedures for producing films containing BaTiO_3 . The most promising methods at this time are the direct occlusion of BaTiO_3 particles from an aqueous basic bath, and the deposition of a material from a hydrolyzed, isopropyl titanate bath containing $\text{Ba}(\text{OH})_2$. Both of these methods can place the material at the anode surface. Further work is necessary to develop a procedure for making a coherent and adherent film. Attempts to reproduce earlier work with the barium acetate-EDTA bath have not produced equivalent films.

The need for additional film evaluation techniques including capacity as a function of temperature and frequency have been discussed.



Section 1

INTRODUCTION

The objective of this investigation is the preparation of high dielectric materials in thin film form on refractory metal substrates. Previous work¹ conducted under contract NASw 765 has explored possible methods of forming films with the Perovskite structure by (1) simultaneous deposition of an insulating oxide and oxidation of the refractory metal substrate and (2) anodization of a suitable metal alloy substrate to produce a composite oxide structure. In cases where the mole percentages of the double oxides are not 50-50, the materials are referred to as doped materials.

The work performed during this quarter has included a partial literature search for data on dielectric properties of rare earth oxides and experimental work in forming titanate films in aqueous and organic electrolytes. Aqueous baths selected and used for film formation on titanium substrates were the following: (1) barium acetate-EDTA (ethylene diamine tetracetate in the form of the disodium salt), (2) barium hydroxide, (3) barium hydroxide-EDTA, (4) barium hydroxide containing dispersed particles of commercial BaTiO_3 , and (5) potassium hydroxide containing dispersed particles of commercial BaTiO_3 . The organic electrolyte consisted of isopropyl alcohol, tetraisopropyl titanate, tetraethyl ammonium hydroxide and a saturated $\text{Ba}(\text{OH})_2$ solution.

Evaluation of the films has been made primarily by comparison of the capacitance using the carbon silver paint counter electrodes.

Section 2

LITERATURE SURVEY

2.1 INTRODUCTION

A continuous monitoring of the recent literature has been maintained in order to keep abreast of pertinent developments. The amount of work being done in related areas is so large that complete coverage at this level of effort is impossible. However, by being selective, a reasonable cross-section can be covered. In addition to the overall dielectric literature interest, two of the specific areas of interest to the present contract have been surveyed. The dielectric properties of some rare earth double oxides have been obtained along with some general information. The applicability of some organic electrolytes has been evaluated and a modified technique of depositing a dielectric material has been proposed.

2.2 RARE EARTH DOUBLE OXIDES

The rare earth elements are capable of forming double oxide species. These compounds have not been characterized as completely as the barium titanate or other Perovskite compounds and thus information about them is not complete. The following classes of compounds have been considered.

(1) $A^{3+} B^{3+} O_3$ Type

A = rare earth configuration element

B = Sc, Ti, V, etc.

(2) MO_2 Mixed Oxides (fluorites) $2\text{A}^{3+}2\text{B}^{4+}\text{O}_7$

A = rare earth such as Ce, Pr, Tb

B = Ti, Zr, etc.

(3) $\text{A}^{2+}12\text{B}^{3+}\text{O}_{19}$ (magneto-plumbite)

A = alkaline earth

B = normally iron; partial or complete substitution by
rare earth metal

The initial literature work revealed that very little electrical information concerning the rare earth oxides is available. The data in Table I is compiled from Landolt-Bornstein. ²

Table I

DIELECTRIC PROPERTIES OF SOME MATERIALS CONTAINING RARE EARTHS

<u>Material</u>	<u>Form</u>	<u>Temperature</u>	
		<u>°C</u>	<u>K</u>
LaScO_3	Ceramic	20	30
NdScO_3	Ceramic	20	27
NdAlO_3	Ceramic	20	17.5
CaCeO_3	Ceramic	20	21
CeO_2	Ceramic	20	26
Ce_2O_3	Ceramic	-	7
Y_2O_3	Ceramic	20	13

The materials listed in Table 2 have been reported to have interesting dielectric properties. Copies of these references have been ordered in order to fill out the sketchy information. At this time none of the dielectric properties reported for these classes of materials are as striking as for the titanates, zirconates, niobates or tantalates.

Table 2

PROPERTIES OF ADDITIONAL RARE EARTH MATERIALS

<u>Material</u>	<u>Dielectric Constant</u>	<u>Ref.</u>	<u>Remarks</u>
$\text{La}_2\text{O}_3 - \text{TiO}_2$	40	6,7,8	
$\text{Ce}_2\text{O}_3 - \text{TiO}_2$	40	6,7,8	
LaGaO_3	None	4,5	Discontinuity of temperature of transition (Curie Point?) 90-100°
CeGaO_3	Reported	4,5	
PrGaO_3	--	4,5	
NdGaO_3	--	4,5	
LaAlO_3	--	4	
NdAlO_3	17.5	4	
La_2O_3		3	

2.3 ORGANIC ELECTROLYTES

Results obtained in this laboratory lead to the tentative conclusion that anodic oxide films grow on titanium by transport of oxygen (or oxygen carrier) through the film to the metal-oxide interface.¹ Thus, other oxides may only be incorporated into the titanium oxidic coating when the coating is porous or grown under such conditions that a polycrystalline coating is obtained. Attempts to incorporate a second oxide such as PbO or SnO while forming a non-porous amorphous anodic film have failed because the titanium oxide is formed first and then a thin conducting coating of the second oxide is deposited on but not in the titanium oxide.

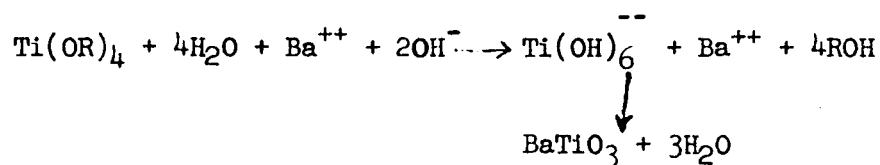
Based upon the results and conclusions, the best approaches seem to be either to form the high dielectric coating by incorporating a high dielectric material into a porous titanium oxidic coating by occlusion of electrophoretically moved particles, or by utilizing a titanium oxide anion to form a titanate on an anode of another metal such as cadmium, lead or barium.

In order to test these approaches, it is necessary to formulate a system containing the desired anions. Barium titanate of 200 to 500⁰Å particle size has been prepared by solution precipitation techniques ^{9,10,11}. This material has good dielectric properties. ⁹

Q factor at 60 kilovolts/cm.	700
Breakdown voltage of a one mil film	400 volts
Dielectric constant at -40°C	550
25°C	620
150°C	640
200°C	starts increasing

Dielectric constant drops precipitously above 25 volts/mil

These techniques consist of either the addition of water to an alcoholic solution of titanium tetraethylate and barium methylate, or the addition of an alcoholic solution of a titanium ester (e.g., tetraisopropyl titanate) to an aqueous solution of barium hydroxide of pH 11 to 14. A simplified mechanism for the latter technique has been suggested. ¹¹ Based upon the reaction,



they suggest an initial step involving the coordination of four water molecules and two hydroxyl groups through their oxygen to the titanium of the Lewis acid $[\text{Ti(OR)}_4]$ in a nucleophilic process. One of the protons from each of the water molecules interacts with the oxygen of the alkoxide group to split off alcohol. The resulting anion, Ti(OH)_6^{--} , is considered to have a transient existence, stabilizing by undergoing condensation-polymerization with the release of water to form an infinite three-dimensional array of

TiO_6 octahedra linked to six others through their corners. Since there are no discrete anionic groups in BaTiO_3 , the condensation-polymerization is such that Ba + 3O together form a cubic close-packed arrangement in the TiO_6 array.

The hydrolysis of the titanate esters presents a unique opportunity of preparing a bath which contains titanium in the anionic form. If the $\text{Ti}(\text{OH})_6^{--}$ ion or any hydrolysis ion is stable in a basic bath, then a method of preparing titanates should be possible. One approach would be the anodization of a cadmium or lead anode in the ester to form the appropriate titanates. Another possible method uses the basic isopropyl titanate bath with additions of barium hydroxide or other alkaline earth hydroxides. This latter bath could produce either a precipitate of the alkaline earth titanate which could be transported electrophoretically to the anode if charged correctly or a soluble titanate complex which would be electrochemically deposited.

Section 3

FILM PREPARATION AND EVALUATION

3.1 GENERAL EXPERIMENTAL PROCEDURE

All electrolyte constituent materials used have been reagent grade. The BaTiO_3 was obtained from the TAM Division of National Lead. Metal substrates were cut from 5 or 6 mil sheets of Ti 75A or the alloy, Ti6Al4V, both of which were obtained from the Titanium Corporation of America. Cadmium and lead were cut from sheets of 99.95 and 99.90% purity, respectively.

Surface preparation of the titanium has been standardized as a 3 to 5 sec dip in an etch consisting of 10 ml 48% HF, 60 ml 30% H_2O_2 , and 30 ml H_2O . The metal is washed in a stream of H_2O upon removal from the etch and dried with laboratory chemical wipes. The cadmium is etched for 30 seconds in 40 ml acetic acid-30 ml nitric acid bath and then quenched in concentrated acetic acid and rinsed in H_2O . The lead anodes are etched in concentrated nitric acid and rinsed in H_2O .

Following anodization the films are routinely rinsed with distilled H_2O and dried at 110°C . Counter electrodes are applied using Aquadag No. 194 as a base and applying a silver paint duPont No. 6730 on the dried Aquadag. Drying is done at 110°C for 1/2 hour. All measurements are reported in terms of series capacitance.

3.2 EXPERIMENTAL RESULTS

3.2.1 OBJECTIVE

During this quarter the laboratory experimental work has been directed toward developing high dielectric films of the titanate type. The objective has been sought by three different approaches utilizing both aqueous and organic electrolytes. The approaches include the decomposition of a complex and the occlusion of particulate barium titanate in the anodic film.

Improvements in several evaluation techniques have been sought. Most vitally needed is a film thickness technique that is sufficiently precise to warrant use in dielectric constant calculations. Other evaluation techniques being considered include capacity measurements as a function of temperature and signal frequency.

3.2.2 OCCLUSION OF PARTICULATE HIGH DIELECTRIC MATERIAL

Experiments conducted during the first year of this study indicated that electrophoretic deposits of BaTiO_3 could be made from several baths. However, the typical properties of electrophoretic coatings were observed in that they lacked good cohesion and adhesion. Attempts to improve these properties were not successful.

A technique recently developed at this laboratory under NASA contract NAS 8-1585 and NAS 8-11117¹² was selected as a possible technique in forming high dielectric films. This technique is basically an anodization of the substrate in a slurry of the desired particles in an appropriate anodization bath. The details of the fundamental processes involved have been discussed in the reports under that contract. A general description is as follows. In order to promote the migration of particles suspended in a bath, certain cation

concentrations, notably H_3O^+ , must be reduced to a low level. The refractory oxides and probably most refractory silicates and aluminates assume a positive charge in acid solutions due to the adsorption of these ions. In order to neutralize and make the particles negatively charged, it is necessary to use a basic solution. In basic solutions the hydroxyl ion is adsorbed and the particles are made negative in charge. Thus, the particles can then be attracted to the anode which is positively charged. Along with the above requirement, it is necessary to exclude certain anions which promote the transfer of electricity through the solution by other methods. Included in this class are the anions sulfate and chloride.

The system used in developing this technique was a slurry of TiO_2 or ZnO in a bath containing dissolved sodium aluminate. The substrate materials used were aluminum and aluminum alloys. Coherent and adherent coatings were obtained whose reflectance spectra showed the presence of the particular oxide used. The transition from those experiments to the present anticipated system involves both a change in substrate and a change in dispersed material from a simple oxide to a double oxide.

Three baths have been used in some preliminary attempts to find an approximate applicable system. The bath compositions are found in Table 3.

Table 3

BATH COMPOSITIONS FOR DIRECT OCCLUSION PROCESS

Bath No.	Concentrations g/l			
	KOH	Ba(OH) ₂	NaAlO ₂	BaTiO ₃ ⁽¹⁾
35-143	--	--	2.5	50
11-3	--	--	1.0	--
11-4	--	--	1.0	80
35-138	--	10	--	50

(1) BaTiO₃ is dispersed as a solid in the bath.

Table 3 (Cont'd)

Bath No.	Concentrations g/l			BaTiO ₃ ⁽¹⁾
	KOH	Ba(OH) ₂	NaAlO ₂	
35-139	1.0	--	--	10
35-140	1.0	--	--	20
35-148	1.0	--	--	--
35-149	1.0	--	--	10
11-2	1.0	--	--	80
11-9	100.0	--	--	200

(1) BaTiO₃ is dispersed as a solid in the bath.

The results of these anodizations are as follows:

- In all systems with low base concentrations, a thin, non-porous, transparent film showing interference colors is grown upon which a thin layer of BaTiO₃ is deposited. The layer of BaTiO₃ is not adherent or coherent when dried.
- The capacitance data obtained on those samples to which a counter electrode could be applied on the BaTiO₃ was the same as the capacitance data obtained for the clear, interference films formed in identical baths without BaTiO₃ present (about 0.025 u f/cm²).
- However, samples formed in the 10% KOH bath, bath 11-9, have shown surprisingly different characteristics. When current densities of 40 ma/cm² or greater are used, a gray, white film is formed which is adherent and coherent upon drying. Preliminary capacitance values of 0.35 u f/cm² have been obtained.

The last results obtained are very encouraging. From this preliminary data it can be concluded that while some changes in bath composition must be made, a strongly caustic solution containing dispersed BaTiO₃ can be used to form a coating that has a higher than usual capacitance. Whether or not this

coating contains a high dielectric material will be determined when a better description of the coating is available.

3.3 BARIUM ACETATE - EDTA BATH

Earlier experiments¹ have shown that opaque yellow to white coatings are formed on titanium when it is anodized at breakdown potential in baths containing barium acetate and the disodium salt of ethylene diaminetetra-acetic acid. Furthermore, it was shown that by making this bath basic, both barium and titanium were present in the stripped coating in major amounts according to semi-quantitative spectrographic analysis. The capacity values of these films were rather low (10 pico farads measured with Hg counter electrodes) due to the probable lack of crystallinity. At that time several separate baths were used and the results were in agreement.

In the experimental work performed during this quarter, three baths based on the decomposition of a barium complex have been used and are found in Table 4. The capacity values indicated are averages for several samples. The spread of values is not greater than $\pm 20\%$. Some larger variations are produced by varying current density, time, and temperature. However, these will not affect the general conclusions.

The films formed were transparent interference thin films, and these provide the higher capacitance data because of their relative thickness while the lower capacity values occur with a thin gray film not at all like the thick yellow to white films reported earlier. In the experiments conducted in this quarter, the yellow to white thick coating has not been produced.

Table 4

COMPOSITION OF BARIUM COMPLEX BATHS

Bath No.	Ba(C ₂ H ₃ O ₂) ₂	Ba(OH) ₂	EDTA	KOH	H ₃ BO ₃	Capacity Range <i>μf/cm²</i>
11-1	--	30	50	5	--	0.037-0.048
35-136A	22	--	30	10	--	0.034
35-136B	22	--	35	15	--	0.009-0.034
35-137	22	--	30	20	5	0.0016-0.009
35-144	22	--	30	20	5	0.0032-0.0052
35-145	22	--	30	10	--	0.021-0.082
35-146	22	--	36	25	--	0.038-0.069

3.4 ORGANIC ELECTROLYTE EXPERIMENTS

Some initial experiments were performed in which titanium was made anodic in an acetic anhydride bath developed in this laboratory for the anodization of germanium.¹³ The electrical properties of capacity and loss were similar to those observed for titania films made in aqueous baths. Rather than approach the anodization of titanium in an organic electrolyte in a conventional manner, a fresh approach utilizing a combination of electrophoresis and anodization was proposed. This approach outlined earlier utilizes techniques developed for the preparation of high dielectric material. The technique consists of hydrolyzing the isopropyl titanate ester in isopropyl alcohol. This can be done with or without the presence of barium hydroxide and tetraethyl ammonium hydroxide. Several different bath compositions have been used and are found in Table 5.

The cadmium was used as an anode initially because CdTiO₃ has a fairly high dielectric constant and does not react with the bath as barium metal would.

Table 5

COMPOSITIONS OF SEVERAL MIXED ORGANIC-AQUEOUS ELECTROLYTES

Bath No.	Isopropyl Alcohol ml	Isopropyl Titanate ml	Ba(OH) ₂ mg	Tetraethyl Ammonium Hydroxide ml	Current Density ma/cm ²	Final Voltage Volts	Time min.	Anode Material
43-7	35	1	--	5	3 to 50	160 to 250	5 to 120	Cadmium
43-8	35	1	10	5	4 to 20	50 to 280	3 to 15	Cadmium
43-9	42.5	1.5	82.9	7.5	1 to 20	150 to 280	3 to 20	Cadmium
43-10A	35	2	30	5	10 to 100	210 to 280	2 to 12	Cadmium
43-11A	35	5	30	15	10 to 100	110 to 200	4 to 15	Cadmium
43-12	35	2	--	15	6 to 260	120 to 400	1 to 75	Cadmium
43-13	35	2	30	5	3 to 20	300 to 400	6 to 83.3	Cadmium

The lower and upper temperature ranges for $K = 500$ should be -213°C and -153°C instead of the values reported in Ref. 1. Indirect evidence outlined in the next paragraph indicates that a complex of titania or barium titanate is formed. In future work the experiments will use titanium and/or zirconium anodes.

The dissolving of the initial precipitate formed when tetraethyl ammonium hydroxide is added to alcoholic solutions of tetraisopropyl titanate suggest the solution of $\text{Ti}(\text{OH})_6^{--}$. The material deposited at the anode from such solutions have been analyzed by x-ray. The results for one sample indicated about 40% crystalline material. This crystalline material was composed of about 60% rutile TiO_2 and 40% anatase TiO_2 . Further work with inert and other anode materials (e.g., Cd, Pb, Pt) is desirable to completely evaluate this technique.

It has been found that, for low to medium concentrations of the above basic solutions, the addition of barium hydroxide (aq. solution) results in the formation of a precipitate which then redissolves. Since the conductivity of this solution has been found to be greatly decreased, it is suggested that:

- (1) a complex hydroxyl anion of BaTiO_3 is obtained,
- (2) an extremely small negatively charged particle of BaTiO_3 is formed, or
- (3) an uncharged molecule or positively charged particle or molecule is formed.

Other work in this laboratory indicates that the third hypothesis is unlikely.

These barium-containing solutions should be tested over a broad range of conditions, including conditions such that the precipitate is partially re-dissolved. The tests should include both anodes which are themselves anodized (e.g., Ti, Cd, Ba, Pb) and anodes which are electrochemically inert (e.g., Pt, Au).

3.5 FILM EVALUATION

The measurement of film thickness has presented a problem during this quarter. The films grown by most of the techniques used are not of the clear transparent type. Attempts to measure the thickness by color interference methods are thus not applicable even if the thickness is small enough. Measurement of film thickness with a commercial Dermatron film thickness meter has not given reliable results. The measurements all indicate that the films are less than 0.5μ thickness. While this problem is not the most critical one at this point in the study, it will be at a later date of the study when the evaluation of the dielectric constant of the films will be desired. Meanwhile techniques to measure the thickness of opaque films will be reviewed and a selection of applicable approaches will be made.

The use of the capacitance-loss factor measurement as a minimum evaluation technique does not lead to unambiguous conclusions regarding the relative merits of the films. The ambiguities occur because in actual measurements the capacitance is dependent upon thickness and porosity of the films. This latter factor is evident from the difference in measured capacity of a film when different counter electrodes are used. The systems presently under evaluation can be further defined by three additional measurements of capacity. One of these is the measurement of capacity at several different temperatures, making sure to include a temperature around the transition range. A second evaluation will include capacity measurement at 1 megacycle as well as the standard measurement at 1 kilocycle. A third evaluation will be a wet capacitance measurement using an inert electrolyte. The last two measurements should provide some estimate of the porosity of the films. In experiments where the inclusion of BaTiO_3 in the anodic film is being studied, the first evaluation technique should be helpful in detecting the presence of significant amounts of the high dielectric material.

The inclusion of these measurements should be of great assistance in selecting the most promising film formation techniques. In addition they will yield additional data of interest to the evaluation phase of the program.

Section 4

PLANS FOR FUTURE WORK

During the next quarter the three processes described in the experimental part of this report will be further evaluated. Emphasis will be placed on the direct occlusion process, both the BaTiO_3 -KOH aqueous system and the mixed organic-aqueous system. If these procedures result in high dielectric film formation, they will be then adapted to comparable high dielectric film formation on zirconium and niobium and a rare earth metal.

Preliminary evaluation of molten salt and gas phase anodization will also be performed during the next quarter.

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